eventually become linear. A long oxidation at 170° is shown in Fig. 4. The initially parabolic oxidation became more rapid than parabolic after 100 minutes.

Thus there is some evidence in favor of the film-cracking hypothesis. Further investigation should be made to test it.

Acknowledgment.—The author is grateful to the Office of Naval Research for support of this research.

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CHICAGO 16, ILLINOIS
RECEIVED OCTOBER 12, 1951

On Halsey's New Multilayer Adsorption Equation

BY W. KEITH HALL

In a recent paper,[1] Halsey derived a multilayer isotherm involving the following assumptions: (1) The source of the van der Waals energy, ΔE, has its origin one adsorbate diameter below the center of the first adsorbed layer. (2) ΔE decays with the third power of the distance from the surface. (3) Regions of equal ΔE are localized into large enough patches so that edge effects may be neglected.

The first two of these assumptions are incompatible. The r^{-3} law for van der Waals attractive energy near a surface arises from the r^{-6} law for two isolated atoms or molecules by integrating over the entire volume of the solid, treating it as a continuous medium.[2] In surface chemistry it is usually assumed that the surface "sites" have considerably greater attractive energy than the underlying layers and, if this is the case, the attractive energy could be closely approximated by integration over the surface layer only. This, however, leads to an r^{-4} law. Halsey's use of the r^{-3} law implies that each layer of atoms in the solid has the same attractive power as the surface layer, *i.e.*, the patches of constant energy are piers extending into the solid to a considerable depth. This is in contradiction to assumption (1).

Use of the r^{-4} law would make very little difference in the derivation of Halsey's equation (13), which will become

$$\Theta = \exp\{+\Delta E_0/\Delta E_m\}\sum_{n=1}^{\infty} Z^{n^4} \qquad (13')$$

The series will converge more rapidly, and so the shape of the calculated isotherms, for a given set of parameters, will be somewhat changed in the direction of greater steepness as the liquefaction pressure is approached. The flat portions will become visible at the same relative pressures, but will extend over a greater pressure range and appear at higher values of $\exp\{-\Delta E_0/\Delta E_m\}$.

Alternatively, use of the r^{-3} law requires that one have an exponential distribution of *three* dimensional patches of different adsorption energies, severely restricting the concept of a "site."

U. S. DEPT. OF THE INTERIOR
BUREAU OF MINES
BRUCETON, PA.
RECEIVED OCTOBER 19, 1951

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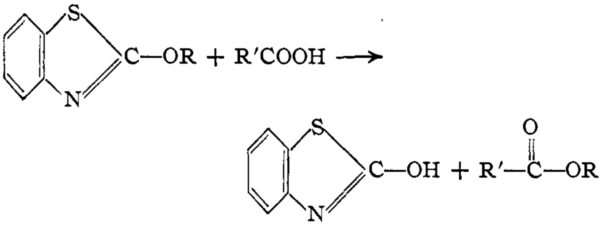
[1] Halsey, THIS JOURNAL, **73**, 2693 (1951).

[2] Brunauer, "The Adsorption of Gases and Vapors," Vol. I, Princeton University Press, Princeton, N. J., 1945, p. 205.

The Effect of Some Organic Acids on Alkyl Heterocyclic Ethers

BY HENRY GILMAN, KENNETH E. LENTZ AND JOHN A. BEEL

The cleavage of 2-alkoxyquinoline and 2-alkoxybenzothiazole compounds by aryl thiols at 170° to form 2-hydroxy derivatives of the heterocycles and alkyl aryl sulfides has recently been reported.[1] We have now carried out further investigations of this reaction in order to determine the effect of varying strengths of acids. In this study the only acids which effected a cleavage similar to that of the thiols[1] were carboxylic acids. Thus, acetic and benzoic acids reacted with 2-ethoxybenzothiazole (I) and 2-benzyloxybenzothiazole (II) to form 32 to 85% yields of 2-hydroxybenzothiazole (III) and the corresponding esters. Oxalic acid has been shown to react similarly with alkyl aryl ethers.[2]



III, R = C_2H_5-, $C_6H_5CH_2$-
R' = CH_3-, C_6H_5-

Phenolic analogs of the thiols, phenol, *p*-cresol and *β*-naphthol, did not cleave I or II, and in most instances the recovery of starting material was high. However, no II was recovered in the reaction with *β*-naphthol even though no cleavage products were isolated. Following the discovery that these phenols were unreactive, experiments were conducted employing the more strongly acidic *p*-nitrophenol. Again the expected alkyl aryl ethers were not obtained though the recovery of starting material was significantly low. *p*-Nitrophenol has been found to react with piperidinomethyl ethyl ether to give an ortho-substituted phenol.[3]

From our results the *pK*a values of the reagents were not significant. Barbituric acid with a *pK*a value less than that of benzoic or acetic acid (see Table I) was almost completely recovered from the reaction with I. The weakly acidic sulfhydryl compounds exhibited an especial reactivity which has been shown previously in reactions with triethylbismuth and tetraethyllead.[4] Two other compounds, 1,3-diphenyl-1,3-propanedione (*β*-hydroxychalcone) and fluorene were found to be unreactive.

Experimental

Cleavage Reactions.—The heterocyclic ether was mixed in a molar ratio 1:1 to 1:3 with the acidic reagent and heated with vigorous stirring in a dry nitrogen atmosphere for 15 to 48 hours. The 2-hydroxy derivative separated from the reaction mixture on cooling, if cleavage had occurred. Frequently the acidic reagent would separate when there had been little or no reaction. Any solid material was isolated

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[1] G. Illuminati and H. Gilman, THIS JOURNAL, **71**, 3349 (1949).

[2] E. Waser and K. Sander, *Helv. Chim. Acta*, **8**, 106 (1925).

[3] C. Yang, *J. Org. Chem.*, **10**, 67 (1945).

[4] H. Gilman and J. F. Nelson, THIS JOURNAL, **59**, 935 (1937).